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# Microstructure and tribological behavior of tungsten-containing diamondlike carbon coated rubbers

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Tungsten-containing diamondlike carbon (W-DLC) coatings have been deposited on FKM (fluorocarbon), ACM (acrylate), and HNBR (hydrogenated nitrile butadiene) rubbers via unbalanced magnetron reactive sputtering from a WC target in  $C_2H_2/Ar$  plasma. The surface morphology and fracture cross sections of coated rubbers have been scrutinized by high resolution scanning electron microscopy (SEM). The random crack networks formed due to the large difference in the coefficients of thermal expansion break down the W-DLC coatings into segments of a couple of hundred micrometers in size, facilitating good flexibility if the interfacial adhesion between the coating and a rubber substrate is strong enough. The size and density of growth defects in the W-DLC coatings strongly depend on the surface roughness of the rubber sheets. The tribological behavior of uncoated and coated rubbers has been investigated with ball-on-disk tribotest under dry sliding condition against a 6 mm 100Cr6 ball. Uncoated rubbers exhibited a very high coefficient of friction ( $>0.9$ ). W-DLC coated FKM did not considerably reduce the friction because the coating was damaged due to poor adhesion. W-DLC coated HNBR and ACM exhibited excellent tribological performance, and very low coefficients of friction ( $<0.24$ ) were achieved even at high normal load of 5 N. After tribotests, the W-DLC coatings on HNBR and ACM were intact and no serious damage was observed on the wear tracks. © 2008 American Vacuum Society. [DOI: 10.1116/1.2889443]

## I. INTRODUCTION

Rubber seals are widely used in lubrication systems and bearings. With its excellent elasticity, rubber can absorb mechanical impact and is extremely good in sealing. However, rubbers exhibit very high coefficients of friction (CoFs) when sliding against most of the engineering materials. Furthermore, the rubber surface can be easily damaged under sliding condition and tends to adhere on the counterpart. Lubricating oil or grease is often used to reduce the friction of rubbers. Under severe working conditions, however, the lubricants may be quickly dried or degraded and thus fail to function. Furthermore, rubber seals are subjected to severe wear, leading to an increase of clearance, which is often the cause of loss of the function and failure of the lubrication system. Applying a wear resistant coating of low friction is one of the solutions to enhance the performance of the rubber seals. Metallic coatings such as Ti, Cr, Mo, W, and Zr have been deposited on rubbers via self-ion-assisted deposition in order to modify their surface.<sup>1,2</sup> The hydrophobicity of the surface of metal-coated rubber was slightly increased,

but the reduction in the coefficient of friction was not as much as expected ( $<2$  times) and the adhesion of coatings to rubber was rather poor.

Diamondlike carbon (DLC) and diamondlike carbon based coatings have been applied in industry for decades due to their excellent properties such as very low friction when sliding against most engineering materials and low wear (for both coating and counterpart).<sup>3,4</sup> DLC can be deposited via physical vapor deposition (PVD) (for hydrogen-free DLC or  $a-C$ )<sup>5-7</sup> or chemical vapor deposition (CVD) (for hydrogenated DLC or  $a-C:H$ ).<sup>8-10</sup> Few exploratory works have been recently done to deposit DLC coatings on rubbers by both PVD and plasma assisted CVD. Yoshida *et al.* deposited DLC on silicon rubber by femtosecond-pulsed laser ablation of frozen  $C_5H_{11}OH$  target.<sup>11</sup> However, the coefficient of friction of the coated rubber was not determined adequately and instead the friction angle was used in the evaluation. A 30% reduction in friction angle was reported with DLC-coated rubber compared to uncoated one. Nakahigashi *et al.* used rf plasma CVD with  $CH_4$  to deposit DLC coatings on CR, NBR, EPT, urethane, and silicone rubbers.<sup>12</sup> The coefficients of friction of uncoated rubbers when sliding against stainless steel counterparts were reported in the range of 1.5–6 whereas those of coated rubbers were 0.7–1.2. It was stated

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TABLE I. Properties of rubber sheets used in this work.

Rubber	Color	Specific gravity	Max. continuous work temp. (°C)	Max. intermittent work temp. (°C)	Coefficient of thermal expansion ( $\times 10^{-6} \text{ K}^{-1}$ )	Indentation depth at 5 N load ( $\mu\text{m}$ )	Modulus (MPa)	$R_a$ (nm)
FKM	Red	1.9	205	300	160	$155 \pm 4$	9.8	406
HNBR	Black	1.0	125	150	230	$115 \pm 3$	15.2	156
ACM	Blue	1.1	180	200	110	$182 \pm 5$	7.7	932

that the friction of coated rubbers was in the same range with that of Teflon, which is often used as a low friction polymer material. However, from the viewpoint of tribology, such a coefficient of friction is still very high and not preferable for industrial applications. Using the same deposition method, Aoki and Ohtake have successfully lowered the CoF of DLC-coated rubbers to the range of  $<0.4$ .<sup>13</sup> However, at the normal load of 3 N or higher, the coated rubber was damaged. Filtered cathodic-arc deposition in the presence of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$  was also employed to deposit DLC on EPDM, FKM, and silicone rubbers by Takikawa and co-workers.<sup>14</sup> The coatings were reported to have a good adhesion to the rubber substrates and did not peel off when the substrates were bent and stretched by hand, but without quantitative evaluation of the adhesion and with no information on their tribological performance.

In this work, W-containing DLC (W-DLC) coatings were deposited via reactive magnetron sputtering on FKM (fluorocarbon), ACM (acrylate), and HNBR (hydrogenated nitrile butadiene) rubbers. The surface morphology and microstructure of the coated rubbers were scrutinized with SEM. The tribological performance of the coated rubbers was investigated via ball-on-disk tribotests under various normal loads. The coefficient of friction of coated rubbers has been drastically lowered down from above the value of 1 of uncoated rubber substrates. It is found out that the random crack networks in the coating can provide essential flexibility for the coating to accompany large elastic strain of rubber substrates under loading contact, if the interface adhesion is strong enough.

## II. EXPERIMENTAL

FKM, ACM, and HNBR rubber sheets of 2 mm thickness were used as substrate. The deformation resistance of a rubber is one of the important factors influencing the tribological performance of a hard coating on soft and yet flexible substrates. For example, a coating on a less deformation resistant rubber will experience higher deformation and thus higher probability of damage. There has not been an adequate method to determine the "hardness" and modulus of rubbers and, therefore, we have proposed a simple and reliable method to evaluate the deformation resistance and to calculate the modulus of rubbers based on indentation technique.<sup>15</sup> The rubber sheets were glued onto polished M2 steel disks and indented by a 6 mm silicon nitride ball with

CSM Revetest scratch tester. The measured indentation depth can be readily translated into the elastic modulus of the rubber substrates via the following equation:

$$E_2 = \frac{3PRE_1(1 - \nu_2^2)}{4E_1(2Rh - h^2)^{3/2} - 3PR(1 - \nu_1^2)} \approx \frac{3PR(1 - \nu_2^2)}{4(2Rh - h^2)^{3/2}}, \quad (1)$$

where  $P$  is the indentation load,  $R$  is the radius of the indenting ball, and  $h$  is the indentation depth measured under the applied load.  $E_1$ ,  $\nu_1$  and  $E_2$ ,  $\nu_2$  are the elastic modulus and Poisson's ratio of the  $\text{Si}_3\text{N}_4$  ball used and rubber substrates, respectively. Table I lists the physical properties of the rubbers used in this study, the measured indentation depth under applied load of 5 N, and the calculated elastic modulus with  $\nu_2=0.5$ .<sup>16</sup>

Deposition of W-DLC coatings was carried out via unbalanced reactive magnetron sputtering from WC targets in  $\text{Ar}/\text{C}_2\text{H}_2$  plasma. The setup of the sputtering system was described elsewhere.<sup>17</sup> The maximum substrate temperature during depositions was measured on the rear side of the rubber substrates not to be higher than 150 °C. The temperature variation of the coating/substrate during one rotation of the sample carousel was estimated to be within 20 °C in the case of only two targets used and a rotation speed of 2 rpm. The W-DLC coatings include two layers: a load bearing WC layer of thickness of about 300 nm followed by a W-DLC layer with thickness of about 700 nm. The W content of the W-DLC layer is about 20 at. % for all the samples, measured by EDX.

The surface morphology and wear track of the uncoated and coated rubbers were characterized with scanning electron microscope (Philips FEG-XL30) right after the deposition or a tribotest. Cross sections of the coated rubbers were made by fracturing after cooling in liquid nitrogen for 10 min. The uncoated and coated rubber sheets were glued onto 30 mm polished M2 steel disks for tribotests that were performed at room temperature (20 °C) on a CSM high temperature tribometer with ball-on-disk configuration. The counterpart was 6 mm commercial 100Cr6 steel balls of hardness HRC 60–62. All the tribotests were carried out at a constant humidity of  $35 \pm 1\%$  kept with a humidity regulator.

## III. RESULTS AND DISCUSSION

An overview and detailed surface morphology of W-DLC coatings on rubbers are shown in Fig. 1. Random crack net-



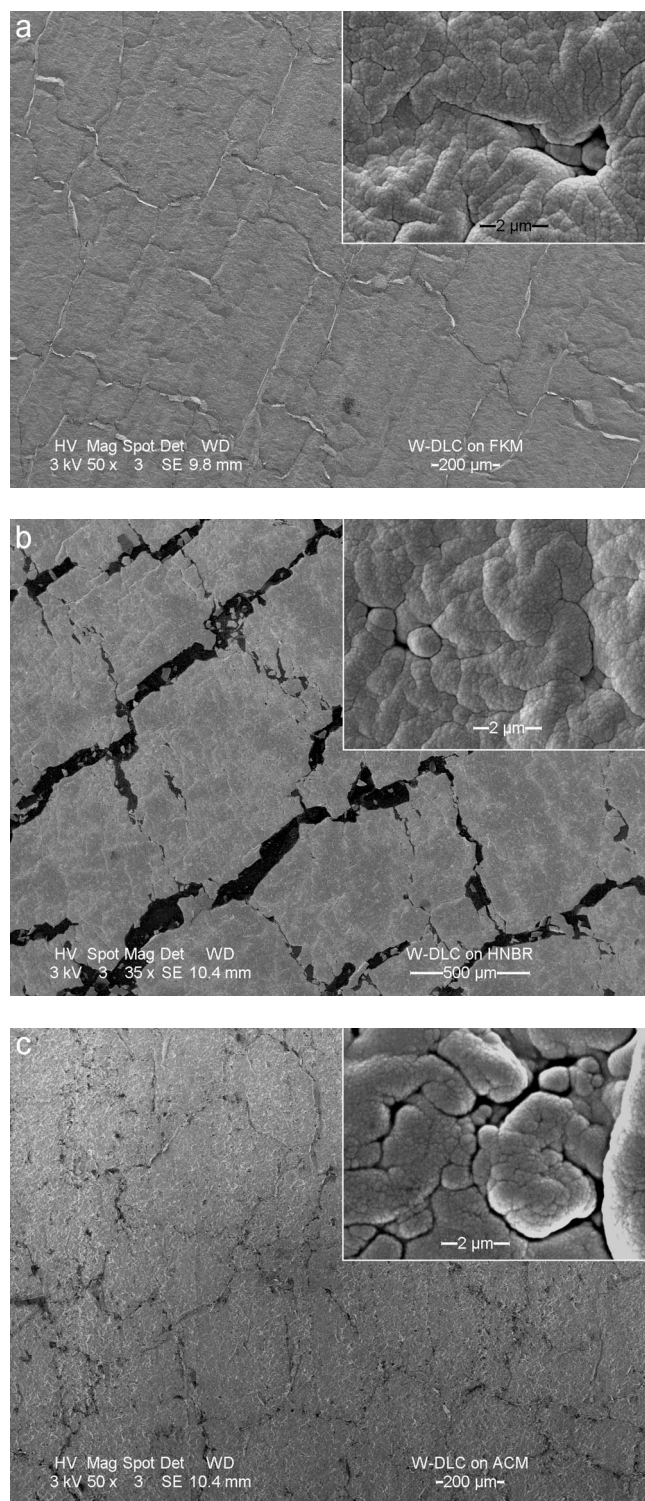


FIG. 1. Surface morphology of W-DLC coated FKM (a), HNBR (b), and ACM (c) rubbers.

works are seen in the coatings. When the rubber substrates passed from one target to another during the deposition, cracks randomly initiated and propagated in the coatings due to the variation of temperature. It is understandable from the large differences in the elasticity and coefficient of thermal expansion between the coating and rubber substrates. The

crack opening of the coating deposited on HNBR is much wider compared to that of coatings on FKM and ACM. The much larger thermal expansion of HNBR ( $230 \times 10^{-6} \text{ K}^{-1}$ ) in comparison with that of FKM ( $160 \times 10^{-6} \text{ K}^{-1}$ ) and ACM ( $110 \times 10^{-6} \text{ K}^{-1}$ ) (see Table I) is likely the main reason for the open cracks as observed. During the cooling process from the deposition temperature to room temperature, the large shrinkage of HNBR made the banks of existing cracks in the coating press each other, bend inwards, and eventually break off in the vicinities of the banks. Consequently, the cracks became widened and open. As an additional evidence, pressing and bending of the crack banks are also observed in the coating on FKM rubber [Fig. 1(a)], but without breaking off due to the moderate coefficient of thermal expansion of FKM rubber. In addition, the coating segments on all three rubbers show a cauliflowertype morphology together with many defects, such as pinholes and gaps between the “cauliflower” branches (see the insets in Fig. 1). These defects are growing defects and their size and density are directly related to the surface roughness of the rubbers. It is well known that interface shadowing is one of the major mechanisms that causes the formation and development of growing defects. A rougher substrate surface enhances shadowing effects and thus more defects nucleate and grow in a coating. Due to the synthesis processes, the surface roughnesses of the rubber sheets are very different from each other. As listed in Table I, the surface roughness of ACM ( $932 \text{ nm } R_a$ ) is much higher than those of FKM ( $406 \text{ nm } R_a$ ) and HNBR ( $156 \text{ nm } R_a$ ). Therefore, many more growing defects are observed in the W-DLC coating deposited on ACM compared to those on FKM and HNBR (see the insets in Fig. 1). In particular, those gaps of tens of nanometers width separate the branches and are expected to contribute a significant strain tolerance and flexibility.

Figure 2 shows the fracture cross sections of W-DLC coatings on three rubber substrates. Both the load-bearing WC layer and the W-DLC top layer exhibit columnar microstructure, with a significant interruption between the two layers. Interfacial delamination often occurs during fracture, leaving a sharp step along the interface on the fracture cross sections. In the case of W-DLC coating on ACM, the fracture cross section clearly demonstrates a growing defect caused by a scratch existing on the surface of the rubber [Fig. 2(c)]. Such defects seem to have positive effects in enhancing the interface adhesion of the coating and especially releasing the stresses. The fracture cross sections also reveal the microstructure of the rubber substrates used in this study: FKM is very dense and glassy whereas HNBR and ACM exhibit grainy structure. It is normal that a polymer containing fluorine is denser than others containing only light elements such as H, C, and N. This explains the nearly doubled specific gravity of FKM (1.9) compared to that of HNBR (1.0) and ACM (1.1) (see Table I).

The coefficients of friction (CoFs) of uncoated and coated rubbers are shown in Fig. 3(a), under dry sliding against 100Cr6 ball counterparts at the sliding velocity of 10 cm/s and normal load of 1 N. Without W-DLC coating, the CoFs

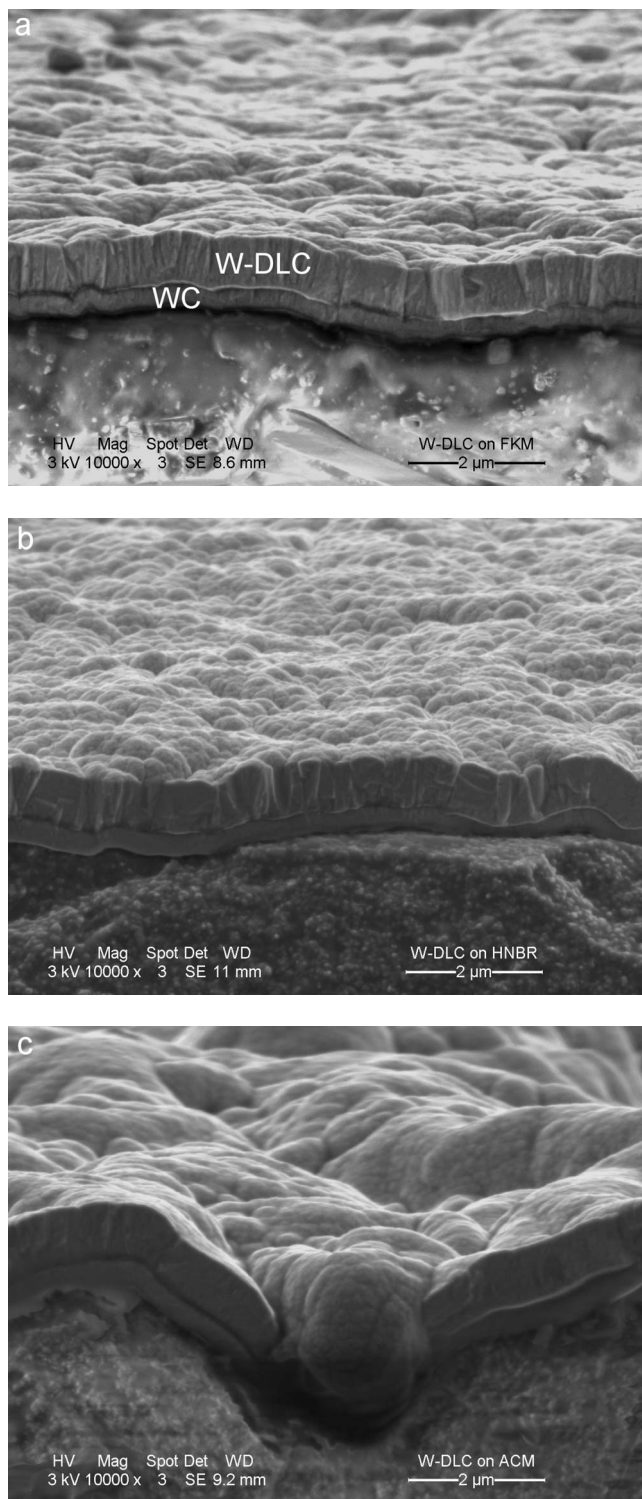


FIG. 2. SEM micrographs showing the fracture cross section of W-DLC coated FKM (a), HNBR (b), and ACM (c) rubbers.

of the rubbers are very high. At the beginning of sliding, the CoFs are about 1.2, 1.9, and 1.4 for FKM, HNBR, and ACM rubber, respectively. The CoF gradually decreases with sliding laps and by the end of the tests reaches steady-state values of 1.0, 1.3, and 0.9 for FKM, HNBR, and ACM rubber, respectively. Such a decrease in friction with sliding is likely

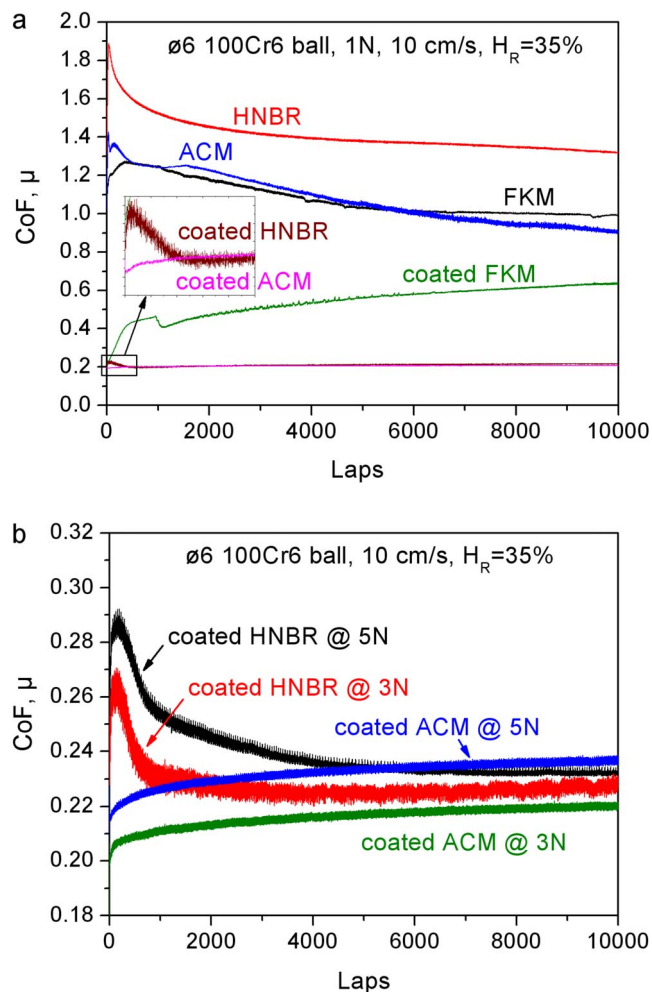


FIG. 3. Coefficient of friction graphs against 100Cr6 steel ball at the sliding velocity of 10 cm/s and relative humidity of 35%: (a) uncoated and W-DLC coated rubbers under normal load of 1 N and (b) W-DLC coated HNBR and ACM rubbers under normal load of 3 and 5 N, respectively.

correlated with the effect of flash temperature rising on the contact area.<sup>18</sup> The observed steady-state CoFs of uncoated rubbers may also be related to the rigidity of the rubber materials. That is to say, the higher the rigidity (elastic modulus) of the rubbers, the higher the steady-state CoF is. With W-DLC coated FKM, the initial CoF is as low as 0.20 and increases gradually with observable fluctuations. By the end of the test, the CoF reaches a relatively high value of 0.63. The fluctuation in the recorded friction curve together with the gradual increase in the CoF indicates a gradual damage of the W-DLC coating during the tribotest. The friction curves of coated HNBR and ACM almost overlay on each other and a zoom-in window of the first 1000 laps is shown for easy distinction. It can be recognized that there is a slight difference in the friction evolution during the first 1000 laps between the coated HNBR and ACM rubbers. The CoF of coated HNBR rubber starts from a value of 0.19 and then quickly increases to the maximum value of 0.23 around 60 laps. After that, the friction gradually decreases and reaches a steady-state value of 0.21 at about 1000 laps. With the coat-



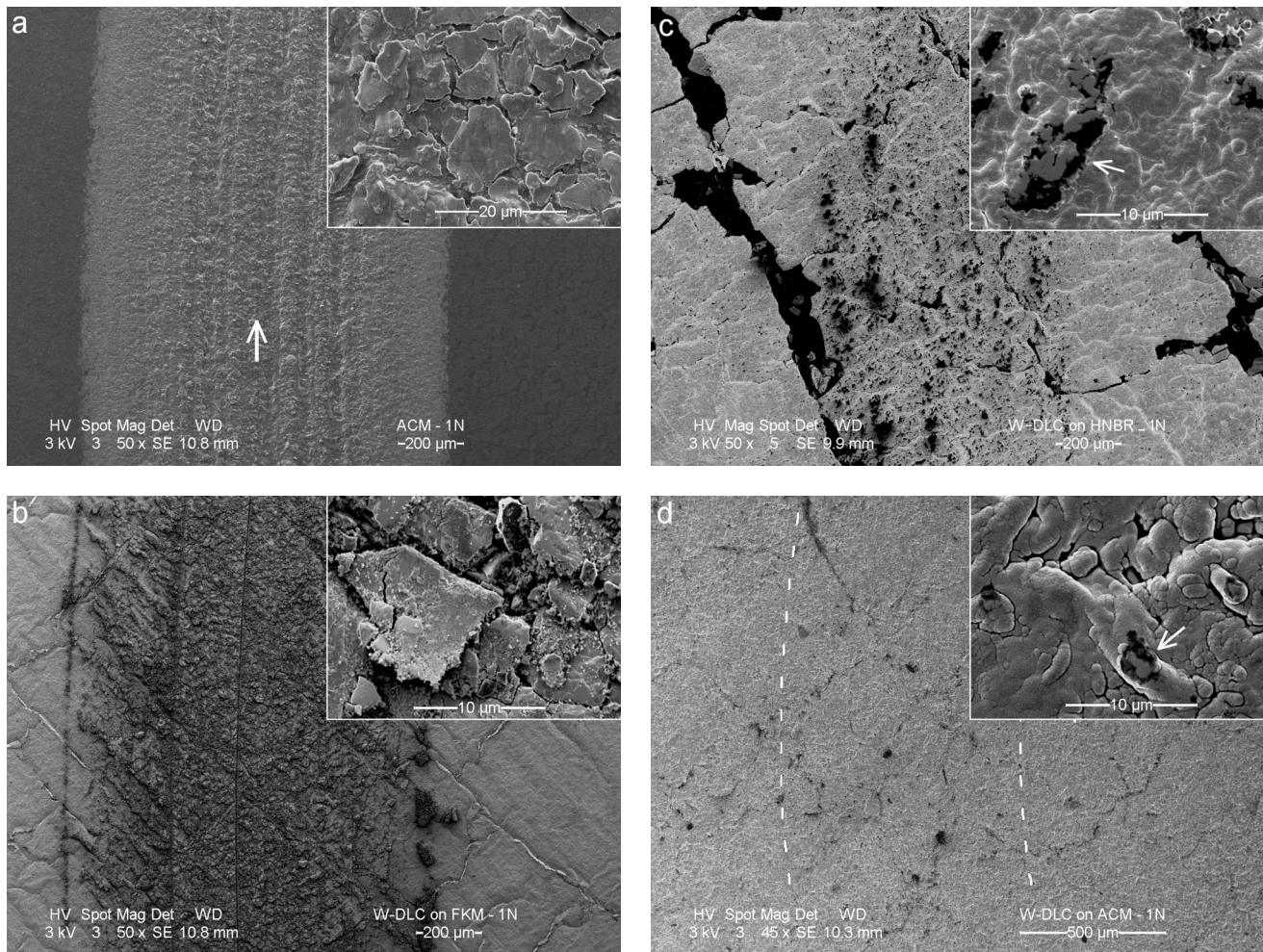


FIG. 4. SEM micrographs showing the wear track of uncoated and coated rubbers sliding against 6 mm 100Cr6 ball counterpart under 1 N normal load for 10 000 laps: (a) uncoated ACM rubber (an arrow indicating the sliding direction of the ball counterpart for all the tests), (b) W-DLC coated FKM rubber, (c) W-DLC coated HNBR rubber, and (d) W-DLC coated ACM rubber with dashed lines indicating the boundaries of the almost invisible wear track. The insets highlight the middle area of the respective wear track.

ing on ACM, the CoF starts from the same value of 0.19 and then gradually increases to the steady-state value of 0.20–0.21 after about 1000 laps. The difference in the initial evolution of CoFs is attributed to the wide open cracks of the coating on HNBR. At the beginning, the sharp banks of the cracks exerted some additional resistance against the counterpart in rubbing. The banks were gradually blunted during the course of sliding and thus a decrease in frictional force. In general, the steady-state CoFs of coated HNBR and ACM rubbers are almost the same: very low and stable during the whole test. Such low CoF values, comparable to that of Me-DLC coatings deposited on steel substrates,<sup>19,20</sup> indicate super tribological behaviors of W-DLC coated HNBR and ACM rubbers and a great enhancement in reduction of friction and wear. The reduction in friction is 4.5 times for coated ACM and that for coated HNBR is more than 6 times. At higher normal loads of 3 and 5 N, the CoFs of W-DLC coated HNBR and ACM rubbers are still very low (0.21–0.24) with a general trend versus running laps similar to the CoFs at 1 N correspondingly, though increased by  $\sim 0.01$  for

each incremental of 2 N normal load [Fig. 3(b)]. Such a behavior is different from the situation of metal-containing DLC coatings on hard substrates where the CoF usually decreases with increasing normal load. The low and stable CoFs indicate that the coatings on HNBR and ACM were well functional in tribotests under the applied loads.

SEM micrographs in Fig. 4 show the wear tracks on uncoated and coated rubbers after tribotests under 1 N normal load. The surface of all uncoated rubbers was damaged after tribotests, evidenced by the observation that a layer distinguishable from the bulk rubber is formed on the wear track [see Fig. 4(a)]. This layer of rubbers was called a “dead layer” with modified properties<sup>18</sup> and formed due to high flash temperatures and high stresses at the asperity contacts between rubber and counterpart during sliding. In fact, the “dead layer” contributes to the reduction of friction of uncoated rubbers in the tribotests as observed in Fig. 3(a). Corresponding to the different frictional behavior of coated rubbers, the W-DLC coating on FKM was fractured and delaminated after tribotest [Fig. 4(b)], whereas the coating



on HNBR [Fig. 4(c)] and ACM rubbers [Fig. 4(d)] was intact and very little wear was observed on a few tiny spots as indicated by arrows in the inset of Figs. 4(c) and 4(d). Compared to the coating on HNBR rubber, the coating on FKM rubber experienced a larger deformation and thus a higher risk of fracture during a tribotest under the same applied load due to the lower modulus of FKM rubber (9.8 vs 15.2 MPa of HNBR rubber). However, it should be noted that the modulus of ACM (7.7 MPa) is even lower than that of FKM, but the coating on ACM was not damaged after tribotest and, in fact, the wear track is almost invisible. Thus, the damage of the coating on FKM is mainly attributed to the poor adhesion of the coating to the glassy surface of FKM rubber substrate. A much denser structure and glassy surface have been observed on FKM rubber, in comparison with ACM and HNBR rubbers which exhibit a grainy morphology and rough surface.<sup>15</sup> It has been proved that the physical linking by interface broadening and interlocking can contribute a significant part to the adhesion of a coating on the substrate.<sup>21,22</sup> The grainy surface of HNBR and ACM rubbers, as also revealed on the fracture cross sections in Figs. 2(b) and 2(c), apparently assigns stronger interfacial adhesion for DLC-based coatings compared to the case of FKM. Also, the growing defects such as the open gaps in the coating on ACM help to relax the stresses and enhance its adhesion to the rubber substrate, leading to an excellent tribological performance observed on coated ACM. In Fig. 4(c), it can be recognized that some tiny spots on the coating on HNBR were abraded and polished. It is believed that the open cracks in the coating [Fig. 1(b)] were likely the main cause. The impact between the ball counterpart and the banks of open cracks caused high local stresses that could further break the crack banks and form fine particles broken from the coating. During sliding, these fine particles acted as abrasive media that gradually abraded and polished the coating. In contrast, the coating on ACM rubber showed only networks of rather closed cracks, and particles were hardly generated during the tribotest so that the wear track was almost invisible because there was no wear.

The optical images of wear scar on the ball counterparts are shown in Fig. 5. Due to a large deformation of the rubber substrates under 1 N applied load, the wear scars are not flat, even along the sliding direction, and their shape is not round as in the case of sliding against the coating on steel or other rigid substrates. The size of the wear scars strongly depends on the rigidity (modulus) of the rubber substrate. That is to say, a smaller wear scar is formed on a rubber of higher rigidity, no matter uncoated or coated. For uncoated rubbers, transfer of FKM and ACM rubbers onto the steel counterparts is observable [Fig. 5(a)], but almost no transfer film of HNBR is seen on the counterpart. The wear scar of the counterpart sliding against coated FKM shows deep scratches [Fig. 5(b)]. As one can envision, the delaminated coating fragments become abrasive particles and scratch the relatively softer surface of the steel ball counterpart, resulting in severe wear of the counterpart and further damage of the coating. On the contrary, the wear scar of the counterparts

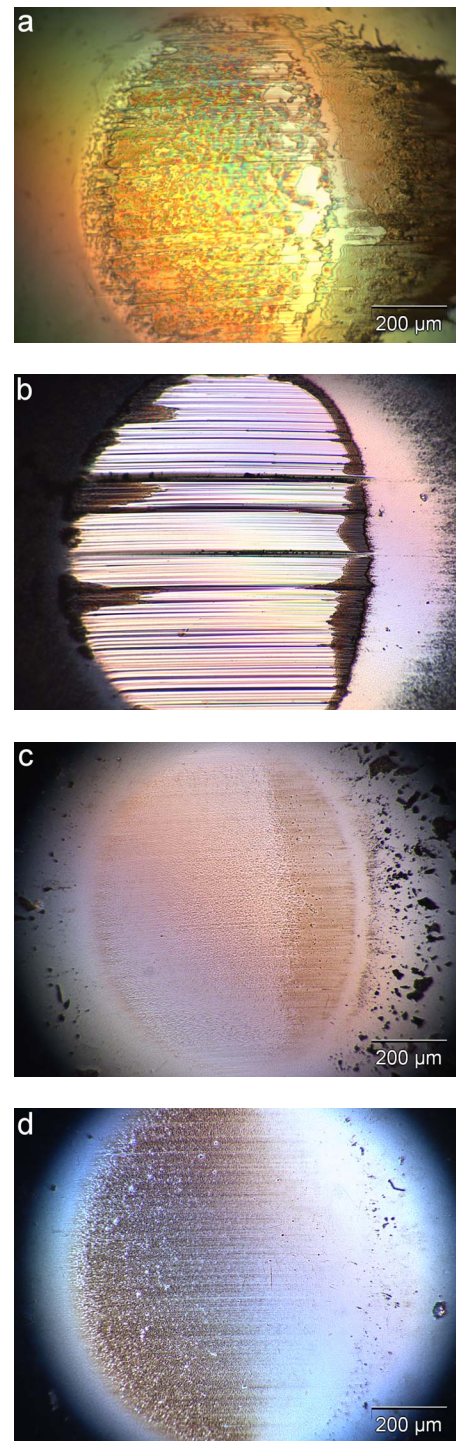


FIG. 5. Optical images showing the wear scar of 6 mm 100Cr6 ball counterparts after tribotests under 1 N normal load for 10 000 laps against uncoated FKM (a), W-DLC coated FKM rubber (b), W-DLC coated HNBR rubber (c), and W-DLC coated ACM rubber (d).

sliding against coated HNBR and ACM is quite smooth and no transfer film is observed [Figs. 5(c) and 5(d)]. This is mainly attributed to the little wear and good adhesion of W-DLC coating to HNBR and ACM substrates.

Under higher applied load of 3 and 5 N, the CoFs of coated HNBR and ACM are still maintained at very low

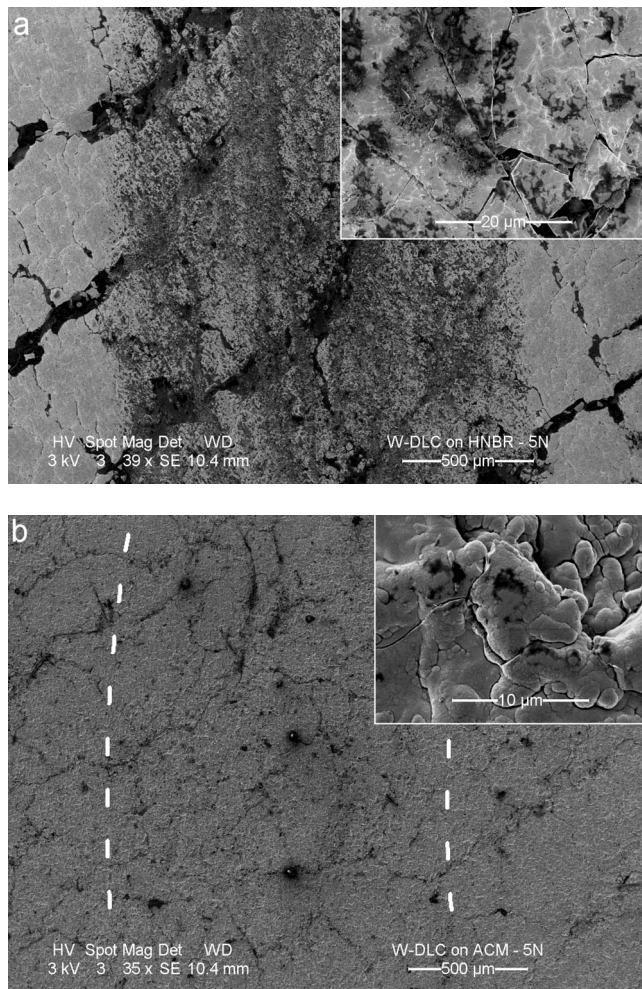


FIG. 6. SEM micrographs showing the wear track of coated rubbers sliding against 6 mm 100Cr6 ball counterpart under 5 N normal load for 10 000 laps: (a) W-DLC coated HNBR rubber and (b) W-DLC coated ACM rubber with dashed lines indicating the boundaries of the hardly visible wear track.

level [0.21–0.24, see Fig. 3(b)], indicating that the coatings on HNBR and ACM were not damaged during tribotests. SEM micrograph of the wear track on the coated HNBR [Fig. 6(a)] reveals that the coating segments adhere well to the substrate after the test of sliding 10 000 laps at 5 N normal load. However, a large amount of abrasive particles were generated from the bank of open cracks and thus more abraded spots are seen on the wear track. In addition, the coating segments started to fracture under such a high normal load [see the inset of Fig. 6(a)]. In order to enhance the performance of W-DLC coating on HNBR, solutions to limit the open cracks should be developed, e.g., use of a ductile interlayer or deposition at a lower temperature. In this sense, it is doubtful whether the segmented coating with large open gaps (close to the diameter of the grid wire) as proposed by Aoki and Ohtake<sup>13</sup> will perform well in contact sliding on dynamic rubber seals, even if its flexibility could be much enhanced. In contrast, the wear track on coated ACM is hardly visible even tested at 5 N normal load, though few coating segments are found cracked together with some tiny

abraded spots seen on the wear track [Fig. 6(b)]. Such a superior wear resistance of the W-DLC coating on rubbers is attributed to the soft contact. That is to say, the peak contact stresses on the asperities are much reduced due to the large contact area that resulted from the large elastic deformation in the rubber substrate and are thus far below the yielding point of the coating. In addition, the thin open gaps between the “cauliflower” branches as shown in Fig. 1(c) facilitate strain tolerance and make the coating flexible to easily follow the rubber substrate. In view of this, a thin W-DLC coating with thickness of a couple hundred nanometers may be thick enough for rubber seals. It should be noted that in the literature the applied loads in the tribotests of DLC coated rubbers were limited to a very low value, normally less than 1 N or even as low as 0.1 N.<sup>12</sup> The reason was that under high applied load the coating would experience serious fracture or peel off due to large deformation of the soft rubber substrates. Aoki and Ohtake reported that at 2.94 N applied load, a sudden jump of CoF from about 0.25 to >1 was observed after 200 laps and the author stated that the coated rubber was fatally damaged due to the high load rather than due to the DLC film peeling off,<sup>13</sup> without showing any micrograph of the wear track. It is inferred that, under such a moderate applied load, the coating had likely been fractured and thus led to the damage of the rubber surface. In our case, W-DLC coatings on HNBR and ACM have not only good adhesion to the substrate but also a certain level of flexibility facilitated by the crack networks, which is crucial for the superb tribological performance observed, even at a high applied load of 5 N.

#### IV. CONCLUSION

The tribological performances of W-DLC (20 at. % W) coated FKM, HNBR, and ACM rubbers were investigated in comparison with uncoated rubbers. Under an applied load of 1 N, uncoated rubbers possessed a rather high coefficient of friction (0.9–1.3) and transfer films of rubber were often observed on the wear scar of the counterpart. As a result, the surface of rubbers was totally damaged, forming a “dead” layer on the wear track. W-DLC coating deposited on FKM did not considerably reduce the friction because of coating damage under sliding contact. The poor adhesion of the coating to FKM is considered as the main reason causing damage of the coating. The fracture and powdering of the coating on FKM caused a severe wear of the steel counterpart. In contrast, coated HNBR and ACM exhibited excellent tribological performance and very low coefficients of friction of 0.20–0.22, 4.5 times the reduction of friction for coated ACM and more than 6 times for coated HNBR. After tribotests, the coatings on HNBR and ACM were intact and a little wear on the coatings was seen. Under higher load of 3 and 5 N, the coated HNBR and ACM rubbers maintained low friction, and no serious damage was observed on the coatings. Such a tribological behavior suggests that the W-DLC coatings on ACM and HNBR rubbers have an effectual flexibility to follow large deformation, facilitated by the crack networks and thin open gaps on the base of good ad-



hesion. The opening of cracks in the coating on HNBR due to high thermal expansion of HNBR should be limited in order to reduce the formation of fractured particles, thus the abrasive wear of both coating and counterpart. In view of the superb wear resistance under soft contact, a W-DLC coating with thickness of a couple of hundred nanometers may be thick enough for rubber seals.

## ACKNOWLEDGMENTS

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